

A COMPELLING EXAMPLE OF SCIENTIFIC INTEGRITY

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Introduction

In recent years, much evidence for fraud and other faults in the conduct of science has appeared. A classic example is *Betrayers of the Truth* (1), in which a critical view is taken of the level of integrity in the scientific enterprise over many centuries and reasons for the failures are assessed. Another, recent example is "Misconduct Accounts for the Majority of Retracted Scientific Publications" (2). This paper in the *Proceedings of the National Academy of Sciences* focuses on the biomedical literature, where the incidence of fraudulent activity seems to be most severe. News accounts in the popular press and in scientific publications such as *Science*, *Nature*, and *Chemical and Engineering News* supply reports of fraud in science (3). Revelations of misconduct in science would naturally tend to cause the public as well as scientists to lower their estimations of the integrity of all scientists.

Because of the conventions about reporting scientific results, it is almost impossible to find clear-cut examples of high levels of integrity being exhibited by scientists. Such examples cannot be found by reading the journals because scientists are inhibited by literary convention and scarcity of journal space from telling the full story about how a project evolves. The majority of scientists sustain high standards without making this practice known explicitly in their papers or in other ways. This silence is regrettable, especially in the face of all the questioning of integrity in science. There is a critical need for positive examples.

Scientists who receive funding from the National Science Foundation and the National Institutes of Health are required to give instruction in ethics to student and postdoctoral researchers. Such presentations are principally admonitory in that they tell about proper scientific ethics and give negative examples of fraudulent work. Largely unavailable is an inspiring component that leads young scientists to high standards of conduct through reading about work done with obvious integrity. Our paper provides a compelling example of a high level of scientific integrity. We hope that publication of this paper on scientific integrity might encourage other examples of exemplary ethical behavior to be brought forward, which could also be used inspirationally in ethics courses. IWL knows of this need from direct experience in teaching ethics courses at the NIH. Through consultation with scientific colleagues we have confirmed this need.

Having in our files and in the Archives of Oberlin College an outstanding example of a case of notable integrity in the practice of science, it seems timely to report about it. The example dates back to the time around 1980 and concerns a topic of great interest at the time.

Experimental Background

First, we recall the circumstances that led to the example. While NCC was on a year's leave in 1978-79 in IWL's laboratory at the National Institutes of Health, we reexamined the literature on the vibrational spectroscopy of the two isomers of diazene (HN=NH), also named di-imide. Many studies had been published about the

infrared and Raman spectroscopy of the trans isomer, even though its short lifetime at room temperature made such studies difficult. Most of the studies were with matrix-isolation methods at very low temperatures, where the reactive trans isomer was stabilized. A few questionable claims of spectroscopic evidence for the cis isomer also existed. The cis isomer was of great interest because it was regarded as the key intermediate in converting atmospheric nitrogen (N_2) to ammonia with the nitrogenase enzyme, as subsequent work has confirmed (4,5). At Oberlin College, we had done a full study of the vibrational spectra of the isotopologues of *trans*-methyldiazene ($CH_3N=NH$) (6), and we had succeeded in converting the trans isomer into the cis isomer by photolysis of frozen material at liquid nitrogen temperature (7). Observing *cis*-methyldiazene was the closest anyone had come to finding direct information about *cis*-diazene. The reinvestigation of the diazenes involved developing a convincing assignment for the six vibrational fundamentals of the trans isomer, based on published matrix-isolation spectra. Normal coordinate calculations using empirical force constants based on the vibrations of the isomers of methyldiazene and *trans*-diazene led to predictions for the vibrational spectrum of *cis*-diazene. These calculations also reinforced the difficult assignment of two close-lying modes of *trans*-diazene, which were separated by less than 30 cm^{-1} . These modes were the antisymmetric in-plane NH bending mode, ν_6 , at 1317 cm^{-1} and the out-of-plane NH torsion mode, ν_4 , at 1288 cm^{-1} .

High-resolution Infrared Spectroscopy at the NRC

The revised vibrational assignment for *trans*-diazene and the predictions for the elusive cis isomer appeared in the *Journal of Chemical Physics* in July 1979 (8). Within a short time of this publication, a letter came from Dr. John Johns at the National Research Council (NRC), the premier laboratory for the physical sciences in Canada. A copy of his letter (Figure 1) follows. Hallin, Johns and Trombetti had done heroic experiments on the high-resolution infrared spectroscopy of *trans*-diazene. They had succeeded in observing the spectrum of this unstable species in the gas phase in a flow system and had assigned 2400 rotational lines in the entangled spectrum in the region where we had assigned the two controversial bands observed in condensed matrix phases. The gas-phase spectrum was made especially complex by a strong

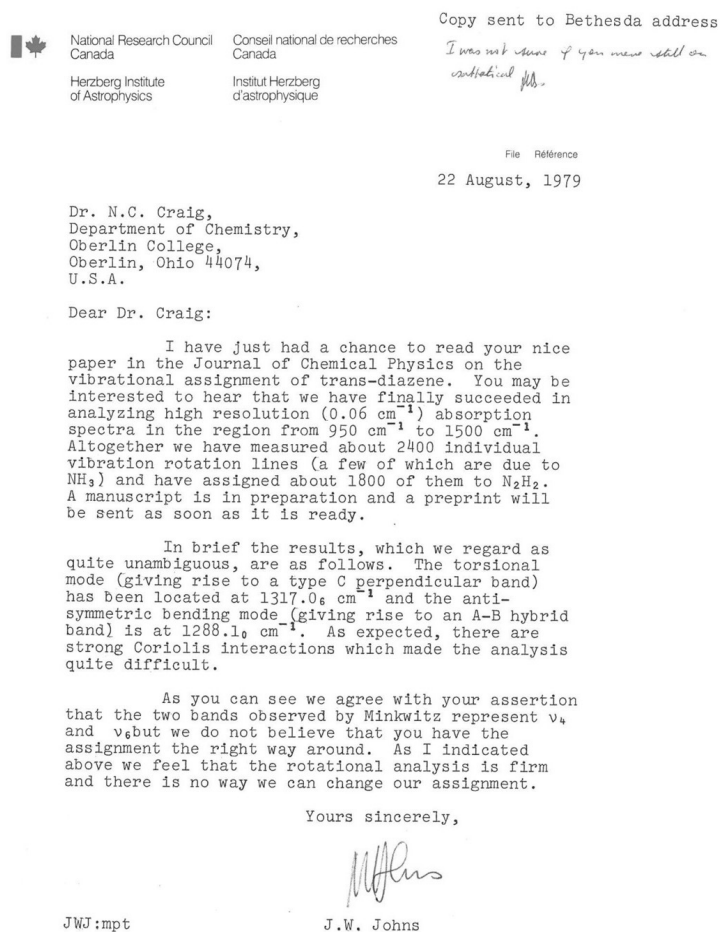


Figure 1. Letter from Johns to Craig pointing out a difference in assigning vibrational modes in *trans*-diazene (9).

Coriolis interaction between the two bending modes and rotational states. Upper rotational states were severely mixed between the two bands. From their analysis of all the rotational structure, Hallin et al. had made an assignment of the two close modes that was opposite to ours. Johns wrote, "...we feel that the rotational analysis is firm and that there is no way we can change our assignment." "A manuscript is in preparation and a preprint will be sent as soon as it is ready" (9).

The evidence for the correct assignment of the two fundamentals from the analysis of the rotational structure seemed superior to what we had done with the various low-resolution spectra and normal coordinate calculations. Even though we had confidence in our analysis, we could do nothing but wish the NRC group well. A copy of our response is in Figure 2 (10).

September 4, 1979

Dr. J. W. Johns
National Research Council
Herzberg Institute of Astrophysics
Ottawa, Canada
K1A 0R6

Dear Dr. Johns:

Thank you for your letter telling me of your elegant results on the high resolution infrared spectrum of *trans*-diazene. Of course, the detailed analysis of the vibration-rotation spectrum gives a definitive assignment. While I was pleased that your results support in general our interpretation of the various low resolution infrared and Raman experiments, I am disappointed that we were unable to get ν_4 and ν_6 in the correct order. No doubt this means that a frequency difference of 29 cm^{-1} is too close to call with the harmonic oscillator approximation applied through the product rule or through normal coordinate calculations to experimental frequencies that include condensed phase values. It is interesting to note that our original prediction of 1326 cm^{-1} for the torsional frequency of *trans*-diazene, which was based on the unambiguous assignment for the NH flapping mode in *trans*-methyldiazene, was so close. Although the ab initio calculations of Peric et al predict a high frequency for the torsional mode of about 1520 cm^{-1} , the value is too imprecise to be of use.

I look forward to seeing the preprint of your paper on *trans*-diazene. Do you have plans to study the high resolution spectrum of the D_2 species?

Since your letter reached me after I got back to Oberlin, I am sending a copy of it and of this letter to Ira Levin at the NIH.

Sincerely yours,

Norman C. Craig
Professor of Chemistry

NCC/md
cc Ira W. Levin

Figure 2. Response from Craig to Johns thanking him for sharing the results of their analysis of the *trans*-diazene spectrum (10).

A Complete Revision

Fifteen months passed, and nothing was heard from the Johns group. In November 1980, Johns sent another letter, as seen in Figure 3. In this letter he reported that he had developed doubts about their analysis and had redone the assignments of the multitude of rotational lines (11). The consequence was a much better fit of the data and a reversal in the order of the assignments of the two modes. Having subsequently done rotational analyses on high-resolution IR spectra of less complicated systems a number of times, NCC testifies to the breath-taking significance of the decision to redo an analysis that must have taken many months. This renewed effort was far from merely tying up loose ends. The paper of K-E. J. Hallin, J. W. C Johns and A. Trombetti had the title, "The Infrared Spectrum of Di-imide near 7.6 mm " (12).

In the paper, there is only one place that hints at the strenuous path leading to the final result. In the section on rotational analysis on p 666, the paper says

Figure 3. Letter from Johns to Craig reporting a reanalysis of the *trans*-diazene spectrum (11).

At this stage we were unable to extend the initial analysis into the region where the asymmetry doubling was resolved. After some time it was finally realized that the vibrational assignment of the two bands could have been made incorrectly because the effect of the strong Coriolis interactions on the selection rules had not been fully realized.

Our response, which is in Figure 4, was muted but congratulatory (13).

It is not hard to imagine a different outcome for these studies. Had the paper from the Johns laboratory appeared first, it is unlikely that anyone would have challenged the conclusion about the proper assignment of the two bending modes of *trans*-diazene. We would certainly have been hesitant about our results. An incorrect assignment of the two fundamentals is likely to have remained in the literature for years.

We emphasize that we bring this compelling example of scientific integrity forward not because we



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Herzberg Institute
of Astrophysics

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d'astrophysique

File Référence

19 November, 1980

Dr. N.C. Craig,
Department of Chemistry,
Oberlin College,
Oberlin, Ohio 44074,
U.S.A.

Dear Dr. Craig:

You will no doubt have wondered what had happened to my paper on *trans* diazene (di-imide). The truth is that I became suspicious of our results and was finally able to show that they were incorrect. This has entailed a complete re-analysis of the data with results that leave me much happier. The big change is that my assignment of the vibrational levels ν_4 and ν_6 now agrees with yours. The new assignment involves different rotational assignments for most of the lines involving values of K_a lower than 3. The resulting parameters are now much more reasonable and they give rise to a fit to the observed frequencies that is almost an order of magnitude better.

For your interest I enclose a preprint of the paper which I have just submitted to the Canadian Journal of Physics.

With best wishes,

JWJ:mpt
Enc:

J.W. Johns

found the correct assignment of the two bending modes of *trans*-diazene. We bring it forward to demonstrate how science takes place at the highest levels of probity. Note that Johns and coworkers undertook their laborious revision in the absence of external motivations such as either compelling evidence or vocal disagreement on our part. We bring it forward because we were privy through correspondence to the high-level path of an investigation in another laboratory.

Another reason for reporting this exceptional example of scientific integrity is to underscore the need for examples of this type. Such material would strengthen instruction in scientific ethics now mandated by the NSF and the NIH. Examples of such material would lift the sights of young scientists. Yet another reason for this report is to encourage scientists to include brief reviews of the evolution of a research project as part of the introduction to a paper.

Acknowledgment

We will be forever grateful to Dr. John Johns for his forthright report of the progress on the analysis of the high-resolution spectrum of *trans*-diazene in his laboratory. He has agreed to the publication of the exchange of letters. Attempts to reach Professor Agostino Trombetti in Italy failed.

References and Notes

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OBERLIN, OHIO 44074

DEPARTMENT OF CHEMISTRY

November 26, 1980

Dr. J. W. Johns
Herzberg Institute of Astrophysics
National Research Council
Ottawa, Canada K1 0R6

Dear Dr. Johns:

Thank you for your letter telling about the revised results of the analysis of the high resolution spectrum of *trans*-diazene and enclosing the preprint. Of course, I am pleased to see that the revision confirms our assignment of $\nu_4(A_1)$ to the lower frequency. In retrospect, I feel that I should have been a stouter defender of that assignment last summer. You deserve hearty congratulations for having the curiosity to reexamine your assignment and the energy to do a painstaking analysis a second time.

A new normal coordinate refinement making use of your Coriolis coupling constants as well as the more secure frequency assignment is in order. Unfortunately, my present normal coordinate programs do not have this capability.

You will be interested to know that we have been working toward a new try at preparing and observing *cis*-diazene at low temperature. Unfortunately, gaining control of the Wiberg method for making clean *trans*-diazene proved quite time-consuming. By the end of last summer we felt that we had solved the synthesis problem. However, we will not be in a position to resume the experiments and try for *cis*-diazene until next summer.

There are a few slips in the manuscript that you should know about. Ackermann is misspelled on pps. 2 and 23; Degradation is misspelled on pps. 7 and 8; and assignment on p. 8. On p. 21 it is said that all of the fundamentals of the *cis* isomer would be active in what is presumed to be the infrared spectrum. Of course, the single A₂ torsion would not be active.

Sincerely yours,

Norman C. Craig
Professor of Chemistry

NCC/ml

Figure 4. Response from Craig to Johns commending the reanalysis of the *trans*-diazene spectrum (13).

About the Authors

Norman C. Craig is Emeritus Biggs Professor of Natural Science in the Department of Chemistry and Biochemistry at Oberlin College, Oberlin, OH, 44074. He has published papers in the *Bulletin* and elsewhere on Charles M. Hall, the inventor of the process for refining aluminum metal. He has also published a paper on Hall's older sister, Julia B. Hall, in *Chemical Heritage*. He has written about the history of chemistry at Oberlin for the *Bulletin*.

Ira W. Levin is a retired Senior Scientist and Scientific Director of the Intramural Research Program of the National Institute of Diabetes and Digestive and Kidney Diseases, National Institutes of Health, Bethesda, MD, 20892. As Scientific Director, he was directly involved with teaching biomedical ethics courses and in leading ethics seminars and discussions for all levels of the scientific staff in his Institutes' program.

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Nominations are open for several posts within the Division of the History of Chemistry (HIST).

If you would like to nominate a HIST member for any of the positions listed below, please contact one of the members of the Nominations and Elections committee by August 1, 2016. Self-nominations are welcome.

Elections will be held later in 2016 for the following positions:

- Chair-Elect (2017-2018), to be Chair in 2019-2020 and immediate past chair in 2021-2022;
- Secretary-Treasurer (2017-2018);
- Councilor (2018-2020 term);
- Councilor (2017-2019 term);
- Alternate Councilor (2018-2020 term);
- Alternate Councilor (2017-2019 term)

The positions and duties are described in HIST bylaws, available at <http://www.scs.uiuc.edu/~mainzv/HIST/bylaws/bylaws-oct1995-HIST.pdf>

One must be a member of ACS AND of HIST to be eligible for any of these positions.

To make a nomination (including a self-nomination) or an inquiry about any of these positions, please contact the chair (Ned Heindel, ndh0@lehigh.edu) of the Nominations and Elections committee by August 1, 2016.

Thank you for your interest and membership in HIST!

Vera Mainz, Sec/Treas HIST
for Ned Heindel, Chair of the Nominations and Elections Committee